



Review article

The role of Copper–Ceria interactions in catalysis science: Recent theoretical and experimental advances

Michalis Konsolakis^{*,1}

School of Production Engineering and Management, Technical University of Crete, GR-73100 Chania, Crete, Greece

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ABSTRACT

Copper-containing cerium oxide materials have received considerable attention both in catalysis and electro-catalysis fields due to their unique physicochemical characteristics in conjunction to their lower cost compared to noble metals (NMs)-based catalysts. Nowadays, it is well documented that the complex Copper–Ceria interactions (either geometric or electronic) have a key role on the catalytic performance. Hence, considerable efforts have been devoted on the understanding and the fine-tuning of metal–oxide interactions. Despite the growing progress in the field, several crucial issues related to the influence of: i) particle's shape and size, ii) active site's chemical state, iii) charge transfer between interfacial sites, and iv) intrinsic defects (e.g., surface oxygen vacancies) on the interfacial activity are still under investigation. This survey summarizes the recent advances in the last 10 years on the fundamental origin of Copper–Ceria interactions and their implications on the catalytic activity. The insights lately obtained by means of: i) *ex situ* advanced characterization techniques, ii) *in situ* sophisticated studies (e.g., *operando* techniques), iii) theoretical analysis (e.g., DFT calculations), and iv) innovative probing approaches (such as the inverse CeO₂/CuO model system) are provided. The state-of-the-art catalytic applications of CuO/CeO₂ binary oxides (water gas shift (WGS) reaction, preferential oxidation (PROX) of CO, CO₂ hydrogenation, selective catalytic reduction (SCR), N₂O decomposition, etc.) in relation to the aforementioned aspects are discussed. Some guidelines towards the fine-tuning of the surface chemistry of CuO/CeO₂ catalysts for real life energy and environmental application are provided.

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* Corresponding author.

E-mail address: mkonsol@science.tuc.gr¹ web: www.tuc.gr/konsolakis.html

1. Introduction

In 1993 Soria et al. [1] reported on the significant interactions between CeO_2 and metal ions deposited on its surface, by employing electron paramagnetic resonance (ESR) spectroscopic studies. They proposed that the formation of oxygen vacancies on the CeO_2 surface facilitated the incorporation of Cu^{2+} ions to the support, whereas at elevated temperature a deeper chemical interaction is produced, which is followed by the agglomeration of copper with a ferromagnetic-type behavior. Later on, Liu and Flytzani-Stephanopoulos [2] introduced the CuO/CeO_2 system for the catalytic oxidation of CO and CH_4 . An extraordinary catalytic activity was recorded, attributed to the strong interaction between the copper and the fluorite-type oxide carrier. Following these pioneering studies more than 1500 articles have been published in relation to the catalytic performance of CuO/CeO_2 catalysts and its origin.

Nowadays, materials consisting of copper and ceria are employed in a wide variety of energy and environmental applications due to their unique catalytic features and lower cost as compared to NMs-based catalysts. In particular, CuO/CeO_2 catalysts have shown great potential as alternatives to NMs for many catalytic applications, involving among others: oxidation of volatile organic compounds (VOCs), water–gas shift (WGS) reaction, low temperature CO oxidation, preferential oxidation of CO in the presence of H_2 excess (CO-PROX), CO_2 hydrogenation toward methanol synthesis, steam reforming (SR) of alcohols/hydrocarbons, selective catalytic reduction (SCR) of NO_x , soot oxidation and nitrous oxide (N_2O) decomposition. Moreover, CuO/CeO_2 catalysts have been widely employed as anode composites in solid oxide fuel cells (SOFCs) due to their adequate electronic conductivity, sufficient electrochemical activity and their resistance to coke formation. Several comprehensive review articles have been already devoted on the applications of CuO/CeO_2 catalysts [3–6]. In this regard, the aim of the present review is to exemplify the fundamental origin of the synergistic metal–support interactions, based on the recent experimental and theoretical advances in the field. Table 1 depicts at a glance the most common applications of CuO/CeO_2 binary system in heterogeneous catalysis along with the commonly considered implications of Cu–Ceria interactions in relation to each process.

Due to the broad range of applications of CuO/CeO_2 catalysts it is of paramount importance to gain further insight into the fundamental understating of Cu–Ceria interactions and their consequences on the catalytic performance. It has been postulated that the intimate contact between CuO and CeO_2 is of essential importance in explaining the remarkable performance of CuO/CeO_2 composites for the aforementioned applications. Moreover, the increasing interest in CuO/CeO_2 system has triggered a substantial research from the theoretical point of view [102,105,119–129]. Nevertheless, the determination of active sites surface structure still consists a challenging task, due to the formation of different interacting species, solid solutions, surface defects (e.g., oxygen vacancies) and electronic perturbations that could coexist in complex supported metal systems under real working conditions.

In the light of the above aspects, the present study aims to shed some light on the fundamental origin of Cu–Ceria interactions and their particular effect on the catalytic performance. Under this perspective, the recent advances lately obtained by means of *in situ* or *ex situ* characterization techniques, theoretical studies and innovative probing approaches (such as the inverse CeO_2/CuO model system) will be presented. The state-of-the-art applications of CuO/CeO_2 catalysts in relation to the above aspects will be outlined. To gain exclusively insight into Cu–Ceria interactions the present review is limited on the studies related to the binary sys-

tem $\text{CuO}-\text{CeO}_2$, ignoring the doping effects that can be induced by various aliovalent modifiers.

2. Copper–Ceria interactions: from SMSI to EMSI?

Cerium oxide or ceria (CeO_2) has been long received increasing attention as a key component in three-way catalytic converters, solid oxide fuel cells, as well as in many industrial and environmental catalytic applications. The wide range of ceria applications can be attributed to its peculiar capability, associated with the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle, to act as an “oxygen buffer” by storing and releasing oxygen under oxidizing and reducing conditions, respectively. More interestingly, many literature studies clearly revealed that the exceptional redox properties of CeO_2 can be further tuned by an appropriate combination with precious and base metals, especially with copper [6,130–134].

It has been well documented that CuO/CeO_2 catalysts demonstrated specific activities comparable or even better to precious metal catalysts for several processes, such as CO oxidation [38], CO-PROX reaction [13], N_2O decomposition [135], etc. The superior reactivity of CuO/Ceria catalysts has been in principle correlated with a synergistic effect linked to strong Copper–Ceria interactions. Several interrelated factors are usually regarded under the general umbrella of “synergism” in order to explain the superiority of CuO/Ceria binary system, involving among others:

- (i) the facilitation of redox interplay between $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couples [136];
- (ii) the presence of defects, such as oxygen vacancies [107,119,131,137,138];
- (iii) superior reducibility of mixed CuO –Ceria composites as compared to that of individual counterparts [107,131,139];
- (iv) the geometric or ligand effects induced by the interaction of metal with the support [136];
- (v) the interfacial reactivity, i.e., the unique activity which give rises at the metal–support interface [136].

In the majority of the studies devoted to CuO/Ceria catalysts, one or more of the abovementioned factors were accounted for their enhanced catalytic activity, without providing, however, the underlying mechanism of these effects. The complexity of the Copper–Ceria interactions in conjunction to the limited availability of *in situ* sophisticated techniques notably hinders the mechanistic understanding at atomic level [140]. Hence, the present review aims to gain insight into the nature and the extent of these interactions based on the state-of-the-art theoretical and experimental studies, which have been obtained in the last years. In the following paragraphs the latest advances regarding the nature of metal–support interactions are summarized.

In relation to the impact of support on the catalytic activity it has been presumed for a long time that supporting carriers, involving reducible oxides, are “inert” materials, providing simply the basis for active phase dispersion. Nowadays, however, it has been well documented – thanks to the rapid development of new generation theoretical and experimental tools – that support is no longer “innocent”. It is now known that metal oxide carriers have a profound influence on the surface properties, which is reflected on catalytic activity [133,136,141,142].

In recent studies by author and co-workers [77,91,143], devoted on the influence of support on the surface and redox properties of Cu-based catalysts, it was revealed that CuO supported on CeO_2 demonstrated the optimum reducibility amongst a series of bare or mixed rare earth oxides (REOs)-based carriers (Fig. 1). More specifically, it was found that the amount of H_2 consumed in Cu catalysts supported on non-reducible carriers, such as Sm_2O_3 and

Table 1Indicative applications of CuO/CeO₂ binary oxides along with the commonly considered implications of Cu–ceria interactions.

Catalytic application	Implications of Cu–Ceria interactions	References
Preferential oxidation of CO in the presence of H ₂ excess (CO-PROX)	excellent redox behavior; formation of surface oxygen vacancies; stabilization of Cu ⁺ active sites; electron exchange between Cu ²⁺ /Cu ⁺ and Ce ⁴⁺ /Ce ³⁺ redox pairs	[7–37]
Water–gas shift (WGS) reaction	formation of reduced copper (Cu ⁺ /Cu ⁰) and cerium (Ce ³⁺) species; stabilization of CO ₂ ^{δ−} species; high H ₂ O dissociation activity	[38–56]
CO ₂ hydrogenation to methanol	formation of active ionic copper species (Cu ⁺); stabilization of active intermediates (e.g., CO ₂ ^{δ−})	[57–61]
Steam reforming (SR)	highly dispersed Cu species; high oxygen mobility; enhanced tolerance to carbon poisoning	[62–68]
Oxidation of volatile organic compounds (VOCs)	enhanced reducibility; high concentration of surface oxygen defects; coexistence of Ce ⁴⁺ /Ce ³⁺ and Cu ²⁺ /Cu ⁺ redox couples	[69–78]
Selective catalytic reduction (SCR) of NO _x	high concentration of surface oxygen vacancies; enhanced reducibility; high population of Cu ⁺ species	[79–87]
N ₂ O decomposition (deN ₂ O)	facilitation of Ce ⁴⁺ /Ce ³⁺ and Cu ²⁺ /Cu ⁺ redox cycles; facilitation of oxygen desorption	[88–93]
CO oxidation	coexistence of Ce ⁴⁺ /Ce ³⁺ and Cu ²⁺ /Cu ⁺ redox couples; excellent reduction behavior; formation of oxygen vacancies; high O ₂ dissociation ability	[38], [94–108]
Soot oxidation	excellent reducibility; high population of surface-active oxygen species;	[109–112]
Fuel cells applications	high electronic conductivity; high concentration of oxygen defects; enhanced tolerance to carbon poisoning	[113–118]

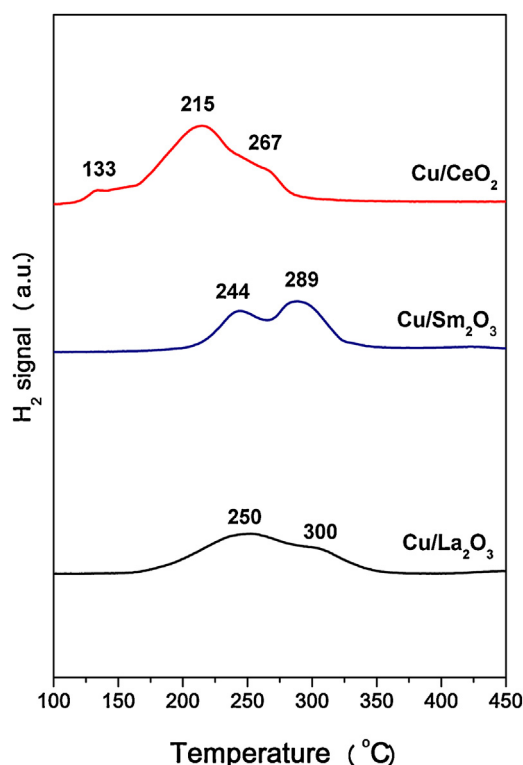


Fig. 1. Temperature programmed reduction (TPR) profiles of 20 wt.% CuO/La₂O₃, CuO/Sm₂O₃ and CuO/CeO₂ catalysts. Indicated peaks are attributed to the CuO reduction along with the reduction of REOs surface oxygen; the low temperature peak at 133 °C is related to the CuO species closely interacting with ceria; H₂ consumption: CuO/CeO₂ (~4.3 mmol/g) > CuO/La₂O₃ (~2.9 mmol/g) > CuO/Sm₂O₃ (~2.5 mmol/g).

La₂O₃, is very close to that required for the complete reduction of CuO to Cu⁰ (ca. 2.5 mmol/g, based on a Cu nominal content of 20 wt.%). Nevertheless, the H₂ amount required for the reduction of CuO/CeO₂ catalysts surpasses the one theoretically required (ca. 4.3 mmol/g), implying facilitation of ceria surface oxygen reduction via strong metal–support interactions [143]. In addition, CuO/CeO₂ samples display a low temperature peak at 133 °C (Fig. 1), which can be ascribed to the reduction of finely dispersed CuO species closely interacting with CeO₂ [91,143]. In a similar manner, it was revealed by means of several complimentary techniques that the amount of oxygen released/uptaken in CuO/CeO₂ exceeded by far that of Cu supported on other carriers, such as Al₂O₃ and ZrO₂

[137,144]. Moreover, the increase of ceria content on CuO/CeO₂ sample notably enhanced the oxygen storage capacity (OSC), due to the higher dispersion of Cu particles and their efficient interaction with cerium species [137].

The significant impact of reducible carriers, like ceria, on the redox/surface properties of metal supported catalysts was in the beginning cover under the so-called SMSI effect (*Strong Metal Support Interactions*), introduced by Tauster et al. in 1978 [145]. The SMSI effect has been well established in a series of reducible supports (such as TiO₂ and CeO₂); at high reduction temperatures the chemisorption ability of metal particles is reduced or even vanished due to the support induced decorating effects [134,146].

However, nowadays it is widely accepted that a variety of mechanisms may be concurrently at work because of metal–support interactions, which can not be fully elucidated by simply considering the SMSI effect. These mechanisms involve primarily the electronic interactions between metal and support, the unique activity of interfacial sites as well as several geometric effects involving the modification of metal sites structural features though their interaction with the support [136,141,147–150].

In this regard, Campbell [149] has recently coined the term EMSI (*Electronic Metal Support Interactions*) to encompass the origin of outstanding catalytic performance, which is resulted as a consequence of the contact between highly dispersed metal particles and reducible oxides, such as ceria. In this concept, the alteration of the chemical properties of metal sites can be considered as the outcome of perturbations in their electronic properties via bonding interaction with the ceria carrier [147,148]. The above hypothesis was experimentally confirmed by several sophisticated techniques, involving among others X-ray crystallography, U–V photoemission spectroscopy, high-angle dark-field scanning transmission electron microscopy (HAADF–STEM), synchrotron X-ray powder diffraction (SXRD) and extended X-ray absorption spectroscopy (EXAFS) [148]. In accordance with the EMSI concept, Acerbi et al. [132] recently found that the reduction temperature of ceria in close proximity to metallic particles strongly depends on the metal's work function. This provides unambiguous evidence of the electronic nature of metal–support interactions [132].

Although the EMSI concept has been mainly adopted to interpret the interactions in precious metal/ceria catalysts, recent studies have established that the same phenomena should be considered for transition metals (TM)/Ceria catalysts, such as Ni/CeO₂ [147]. Senanayake et al. [147], based on a thorough experimental analysis by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), synchrotron-based photoemission (PE), and ultraviolet photoelectron spectroscopy (UPS), proved that the

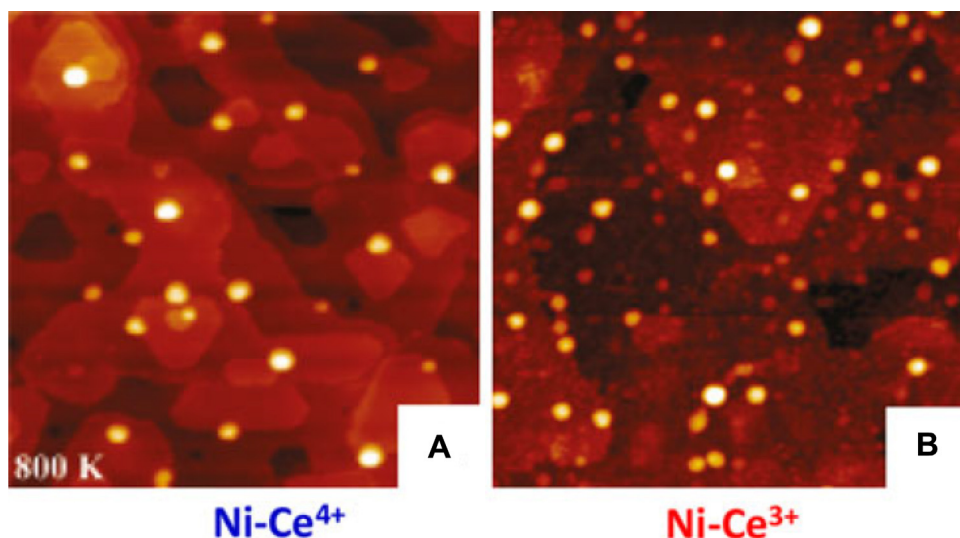


Fig. 2. Scanning tunneling micrographs of Ni nanoparticles (bright dots) supported on a $\text{CeO}_2(111)$ film. A: $\text{CeO}_2(111)$ surface rich in Ce^{4+} with Ni nanoparticles 4.5 nm (diameter) \times 1.1 nm (height) dimension on average. B: $\text{CeO}_{1.77}(111)$ surface composed of a mixture of $\text{Ce}^{3+}/\text{Ce}^{4+}$ with Ni nanoparticles that are of 3.5 nm (diameter) \times 0.8 nm (height).

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Ni–Ceria electronic interactions notably reduce the density of occupied Ni 3d states near the Fermi level. Interestingly, the extent of these interactions is strongly dependant on Ni coverage, *i.e.*, the smaller the coverage, the larger the electronic perturbations on Ni. Moreover, XPS analysis revealed the co-existence of $\text{Ni}^{2+}/\text{Ni}^0$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pairs as a consequence of these electronic interactions. Fig. 2 depicts the STM images of Ni particles deposited on $\text{CeO}_2(111)$ film, where the correlation of Ni particle size with the reduced state of Ce species is evident. These perturbations induced by bonding interactions between Ni particles and CeO_2 carrier resulted in an outstanding activity of WGS and SR reactions (*vide infra*). In a similar manner, Campbell and co-workers have recently shown through a pioneer energetic study that Cu adsorption over $\text{CeO}_2(111)$ surfaces results in a faster decrease of Ce^{4+} compared to Ce^{3+} species, due to the selective binding of Cu adatoms at stoichiometric sites and the electronic interactions between Cu and ceria (transfer of small amount of electron densities from Cu to Ceria) [151]. In view of this fact, Graciani et al. [150] clearly shown, by means of density functional theory (DFT) calculations, that stable Ce^{3+} species can be formed in $\text{CeO}_x/\text{Cu}(111)$ system, as a consequence of the geometric (structural mismatch) and electronic (work function of metal surface) interactions at the oxide–metal interface.

Taking into account that metal particles of various sizes and shapes could be in contact with the oxide carrier under working conditions, a different extent and nature (geometric or electronic) of metal–support interactions should be expected. This introduced a great difficulty to unambiguously reveal the origin of catalytic effects and to establish a definite structure–activity correlation. In a comprehensive study by Pacchioni [141] the interaction of metal particles of sub-nanometer size down to single atoms with an oxide carrier was extensively described. It was concluded, based on the most conceptual aspects of EMSI effect, that as the size of the deposited particles increases the metallic character is recovered, whereas the effect of support is strongly attenuated. In that case the modifications induced by support are limited to the interfacial atoms or the particle's perimeter. However, for metal nanoparticles a direct electronic modification of deposited phase should be considered as a result of the strong electronic metal–support interactions. Moreover, the bonding interactions between metal and oxide can also modify the properties of the oxide, generat-

ing new active sites [150]. Hence, the properties of both metal and oxide entities can be drastically altered at the interface, resulting in a unique interfacial activity. All these aspects, considering the electronic modifications that can be induced by metal–support interactions, will be further discussed in the sequence on the basis of the recent experimental and theoretical advances in the field.

3. Experimental evidences on the Cu–Ceria interactions

On the basis of the abovementioned considerations, it is evident that the fundamental understanding of the local surface structure is a *conditio sine qua non* for establishing a precise structure–activity relationship, which in turn is a prerequisite for the rational design of more effective catalysts. Two different approaches could be applied to gain insight into the structure–activity correlation: i) *in situ* characterization of local surface structure combined with simultaneous study of reaction mechanism, the so-called *operando* studies, ii) *ex situ* characterization of catalyst surface by means of advanced characterization techniques.

Some of the existing techniques are suitable on exploring the surface properties, while some others are better suited for *operando* studies. The techniques which are able to provide surface/morphological information at atomic level do not have the time resolution required for kinetic studies. Moreover, many surface science techniques operate under vacuum conditions, not allowing the *in situ* characterization under reaction conditions. This gap notably hinders the elucidation of surface phenomena (*e.g.*, reconstruction, electronic transitions) taking place under reaction conditions. Therefore, it is necessary to combine advanced surface characterization studies with *operando* studies to understand the origin of the catalytic activity [140].

Fig. 3 illustrates the generally accepted approach for the complete elucidation of catalytic phenomena. The required information, in relation to structure–activity correlation, can be obtained by combining *ex situ* experimental and theoretical studies with kinetic studies and *in situ operando* studies. The recent advances on the *in situ* characterization of heterogeneous catalysts can be found in the comprehensive book “In-situ characterization of Heterogeneous Catalysts”, edited by Rodriguez, Hanson and Chupas [152]. Very recently, Stacchiola [140] reviewed the latest advances on the use of complementary *in situ* techniques at Brookhaven National

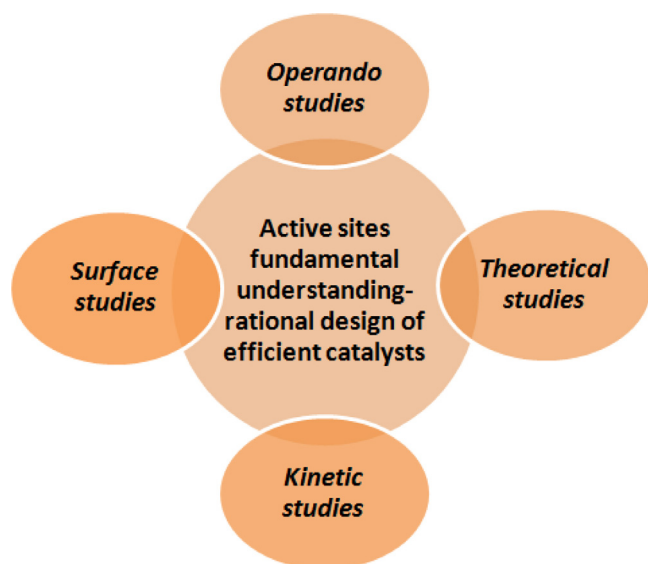


Fig. 3. Required approach for the fundamental understanding of a catalytic process.

Laboratory by investigating model Cu-based catalysts. It was concluded that multifunctional sites, involving partially oxidized Cu atoms and partially reduced Ce atoms, can be formed near the Cu–Ceria interface with subsequent consequences on the redox reaction pathways.

The recent developments with respect to the characterization of CuO–Ceria system by state-of-the-art techniques are provided in the sequence. Pioneering studies by Rodriguez and co-workers, by means of *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), time-resolved X-ray diffraction (TR-XRD) and X-ray absorption spectroscopy (XAS), clearly revealed the important role of metallic copper and oxygen vacancies in WGS reaction over conventional CuO/CeO₂ catalysts [41,42], as well as over well-defined Cu nanoparticles supported on CeO₂ (111) [45,47]. Moreover, Ce L3-edge XANES results indicated the formation of oxygen vacancies and Ce³⁺ species under reaction conditions [41]. These results provided the first documented evidence for a synergistic Cu–O_{vacancy} interaction. In the sequence, the importance of Cu–Ceria interface was established by means of ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) in combination with infrared reflection absorption spectroscopy (AP-IRRAS) over Cu(111) and CeO_x/Cu(111) model systems [43,45–47,153]. Both techniques indicate that under WGS conditions the Cu(111) surface is predominated by CO_{ads} species, contrary to CeO_x/Cu(111) where the stabilization of CO₂^{δ−} species at the interface is revealed. The latter is associated with the extraordinary increase (by more than one order of magnitude) in WGS activity of CeO_x/Cu(111) system in relation to that of Cu(111) (Fig. 4).

More recently, the same research group examined further the role of Cu–Ceria interactions in WGS reaction by means of *operando* XRD, DRIFTS and XAFS [56]. Three nanostructures of CeO₂ with different morphologies (nanospheres, nanorods and nanocubes) were employed as supports (Fig. 5). It was found that ceria defects and imperfections favored strong metal–support interactions, which then have a significant effect on the copper dispersion and particle size. A direct correlation between the size of copper particles and WGS activity was established. The nanosphere ceria-based catalyst demonstrated the best dispersion and water dissociation ability, delivering the optimum performance. In a similar manner, Matolín and co-workers have shown that changes in ceria morphology can lead to a periodic modulation of the electronic structure of Copper–Ceria interface with subsequent consequences

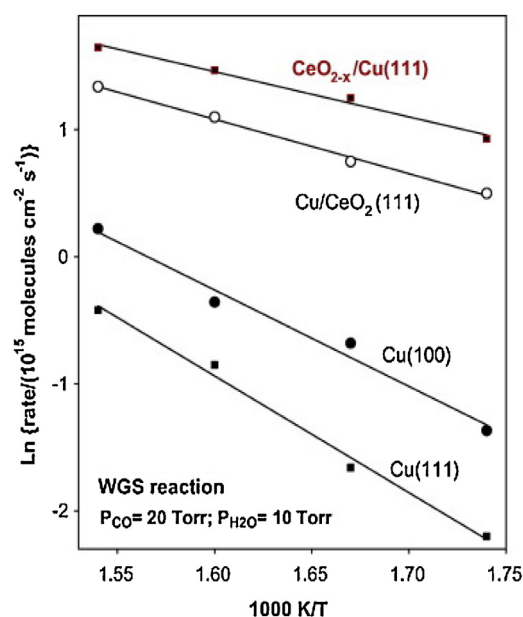


Fig. 4. Arrhenius plot for the WGS reaction rate on clean Cu(111), Cu(100), conventional Cu/CeO₂(111) and inverse CeO₂/Cu(111) system.

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in the catalytic activity [154–156]. Moreover, it was shown that the transition between Ce³⁺ and Ce⁴⁺ states is taking place by the equilibration of mobile oxygen vacancies at the Copper–Ceria interface [156]. Conversely, copper configuration affects both the morphology and the electronic structure of CeO₂ [157]. These results reveal that both CuO and ceria structural/morphological features can affect the electronic structure of interfacial sites, and as a consequence their intrinsic catalytic activity.

Very recently the redox properties and the CO oxidation performance of CuO supported on ceria nanorods was thoroughly investigated by following a multi-technique *operando* approach [103,158]. *In situ* time-resolved X-ray absorption near-edge spectroscopy (TR-XANES) was combined for the first time with DRIFT spectroscopy in the same experimental setup and accompanied with a parallel time-resolved XRD, in order to identify the local surface structure in real time [103]. This combination provided the opportunity to gain insight into the intermediate states during real time transformations [159]. The *in situ* XANES, DRIFTS and MS characterization of CuO/CeO₂ catalysts under reduction by CO is illustrated in Fig. 6. Upon temperature increase a gradual transformation of Cu²⁺ to Cu⁺ and Cu⁰ was observed, revealing the potential of this multi-technique approach to capture the surface modifications in real time. Interestingly, following the same approach over bare CuO, it was shown that CuO reduced more difficult than CuO/CeO₂ catalyst. The observed phenomena were interpreted on the basis of strong electronic Copper–Ceria interactions which favor the CuO reduction via the Ce³⁺ + Cu²⁺ ↔ Ce⁴⁺ + Cu⁺ redox equilibrium.

In a similar manner, Flytzani-Stephanopoulos and co-workers studied the structure sensitivity of CuO/CeO₂ catalysts, prepared by co-precipitation (CP), under WGS reaction by means of XANES [44]. Fig. 7 depicts the steady-state conversion profiles (a) along with the Cu-K-edge XANES profiles (b). It is evident that Cu²⁺ species were dominant at ambient temperature, whereas at elevated temperatures, where the reaction is taking place, they were progressively reduced to Cu⁺/Cu⁰ species. This finding clearly unveiled the key role of reduced Cu sites in WGS activity.

Moreover, the key role of Ce³⁺ species in CuO/Ceria binary system was verified by infrared reflection adsorption spectroscopy

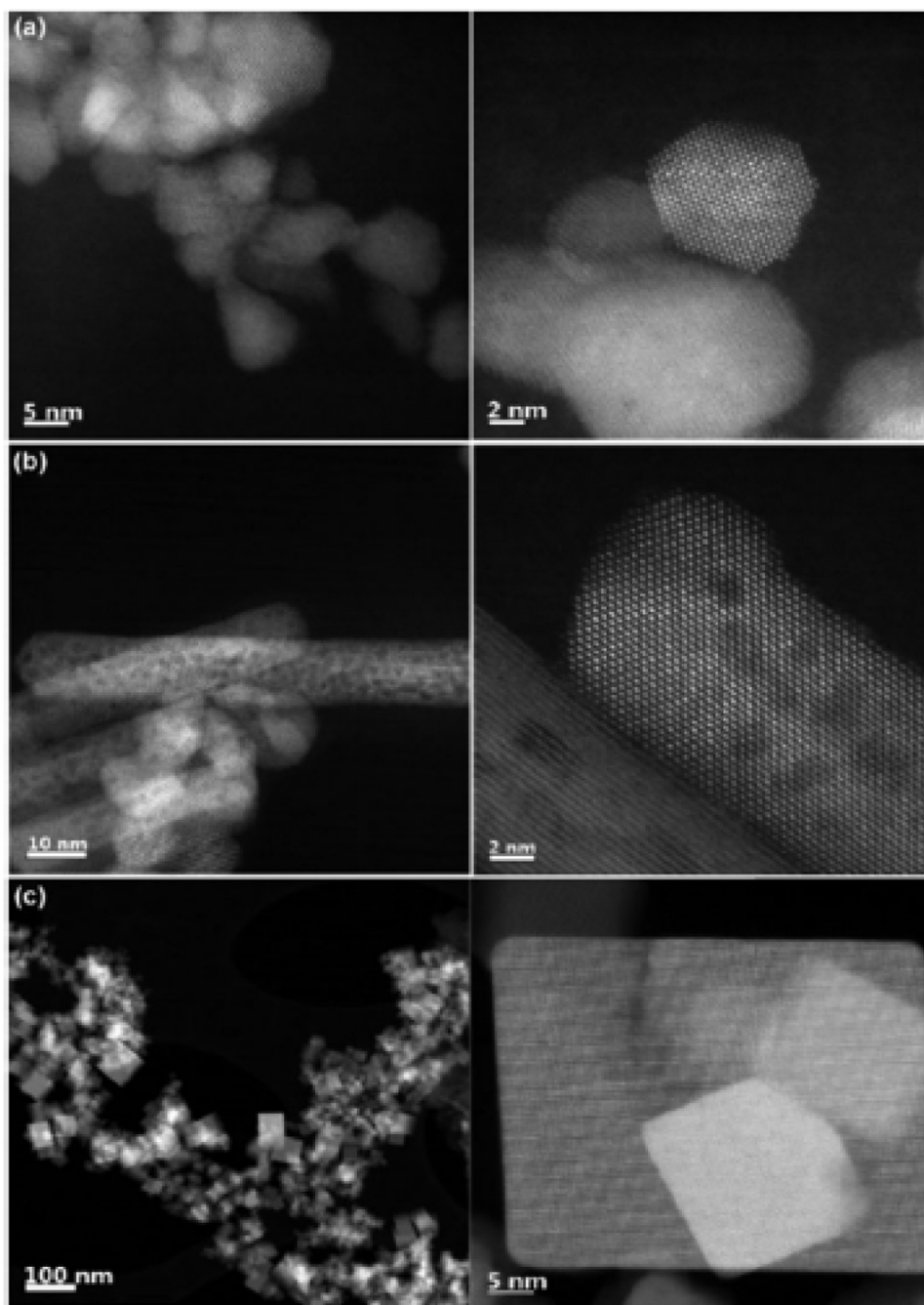


Fig. 5. STEM and HRSTEM images of Cu supported on ceria of different morphology: (a) nanospheres, (b) nanorods, (c) nanocubes.

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(IRRAS) of adsorbed CO on $\text{CeO}_x/\text{Cu}(111)$ [160]. Fig. 8 depicts the IRRAS spectra of CO adsorption for CeO_x films on $\text{Cu}(111)$ imposed to oxidation or reduction pre-treatment. CO exposure to reduced sample results in an intense band at 2162 cm^{-1} , which can be assigned to CO on Ce^{3+} sites. Oxidation pre-treatment leads to the appearance of two low intense bands at 2112 and 2136 cm^{-1} , attributed to the CO adsorption on oxidized and heavily oxidized Cu sites, respectively. At the same time, the intensity of the peak at 2162 cm^{-1} is notably decreased implying the oxidation of Ce^{3+} to Ce^{4+} . *In situ* dilatometric and impedance spectroscopy were also used to explore the thermo-mechanical and electrical properties of nanocrystalline $\text{CuO}_x\text{--CeO}_2$ system [161]. The measurements point to the significant modifications on the electrical and redox proper-

ties of both CeO_2 and CuO that can be induced by Copper–Ceria interactions.

4. Theoretical studies on Cu–Ceria interactions: first principles DFT + U calculations

The intense interest on CuO/Ceria catalysts, and in particular on Cu–Ceria interactions, has stimulated a substantial research from the theoretical point of view. More specifically, the high reactivity of CuO/Ceria catalysts has inspired many theoretical studies on identifying the surface and electronic effects arising from metal–support interface. The latest information with respect to the theoretical studies in catalysis as well as on their contribution to fundamental knowledge and rational catalyst design can be found in a

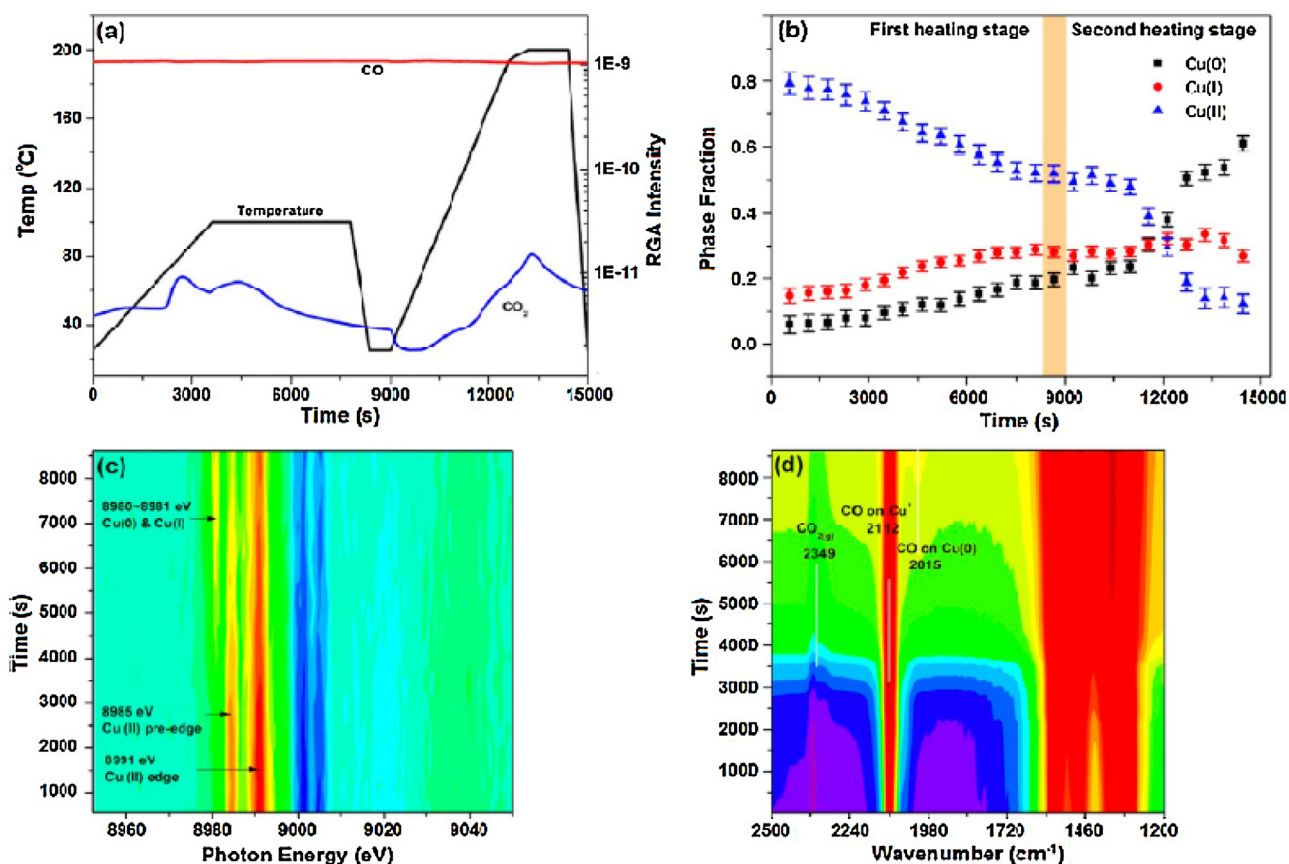


Fig. 6. In situ characterization of CuO/CeO₂ catalyst during reduction by CO: (a) the MS signals for CO and CO₂ evolution, along with the heating temperature profile; (b) linear combination fit (LCF) results derived from XANES data; (c) contour map of the Cu K-edge first derivative XANES spectra, and (d) DRIFTS spectra during the first heating stage.

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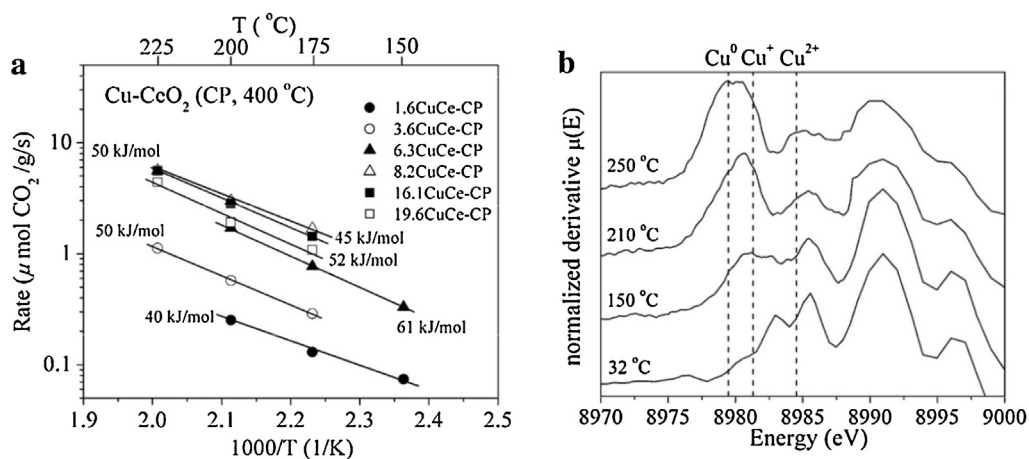


Fig. 7. (a) Steady-state conversion profiles of Copper–Ceria catalysts (χ CuCe–CP, where χ stands on copper content in atomic percent and CP to co-precipitation method) under WGS conditions (2% CO/10% H₂O/He); (b) Cu K-edge XANES profiles of 8.2CuCe–CP catalysts under 5% CO/3% H₂O/He.

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recently published review article by Pašti et al. [122]. In summary, two methods are widely employed within the framework of electronic structure theory: (i) *ab initio* molecular orbital theory (MOT), and (ii) density functional theory (DFT). The latter is more popular taking into account its relatively good accuracy to provide information about the reactivity trend as well as its ability to monitor the electronic structure of complex catalytic systems [122]. However, it is by now established that DFT calculations do not allow the precise

description of reduced ceria (Ce³⁺), where an electron is localized on Ce4f states (e.g., [121,125]). To this end, the addition of Hubbard U term to the energy function (DFT+U calculations), which takes into account the on-site Coulomb interactions, has been proposed in order to capture the structural, electronic and thermodynamic properties of stoichiometric or reduced ceria, even in the presence of metal adatoms or molecular adsorbates [125].

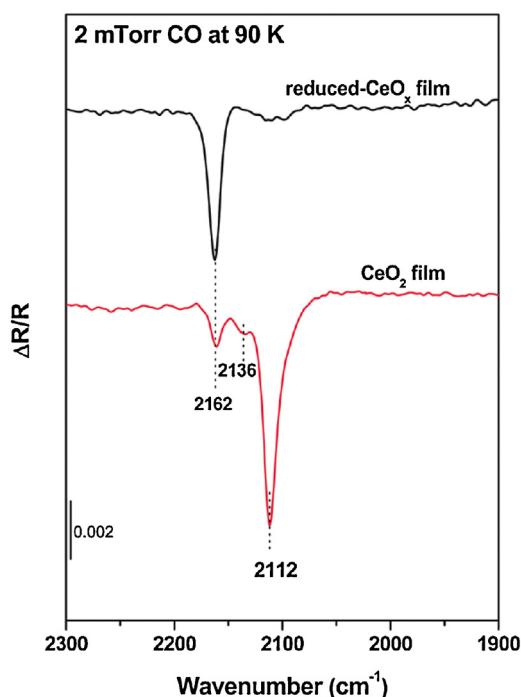


Fig. 8. IRRA spectra collected from reduced- CeO_x and CeO_2 films under 2 mTorr of CO pressure at 90 K. The CeO_2 film was prepared by oxidation of the prepared $\text{CeO}_x/\text{Cu}(111)$ system at 550 K with 5 mTorr of O_2 at 400 K for 10 min. The reduced- CeO_x film was obtained by reducing the CeO_2 film with 2 mTorr of CO at 650 K for 30 min. The band at 2162 cm^{-1} was attributed to CO on Ce^{3+} sites, whereas the bands at 2112 and 2136 cm^{-1} to CO adsorption on oxidized and heavily oxidized Cu sites, respectively.

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The effect of Cu addition to ceria surface has been extensively studied using first-principles DFT+U calculations [105,119–121,123–127,162,163]. The majority of these studies indicated that Cu incorporation to ceria surface is accompanied by a charge transfer process between Cu and neighboring Ce^{4+} species, resulting in CeO_2 reduction (Ce^{3+}). Szabová et al. [125,127] investigated the impact of Cu deposition on stoichiometric and partially reduced ceria films by means of DFT calculations and experimental studies. Copper deposition on the stoichiometric CeO_2 caused an obvious reduction of CeO_2 , as depicted in Fig. 9. The Ce^{3+} contribution is increased from about 1% to 14% over bare ceria at 60°C , in agreement with DFT calculations. In contrast, Ce^{3+} species abundance did not change upon the addition of Cu in reduced ceria surface.

Lu et al. [119] investigated the impact of Cu-doping in ceria by DFT+U calculations, with particular emphasis on oxygen vacancies formation. It was found that both the first and second energy of oxygen vacancy formation (E_{vac}) in Copper–Ceria is smaller compared to bare ceria, indicating that Cu dopant can serve as a seed for the formation of oxygen vacancies. The lowering in E_{vac} upon Cu-doping was in some degree ascribed to the dopant-induced structural relaxation and partly to charge compensations between Cu and Ce species. The latter demonstrates the complex nature of Cu–Ceria interactions, especially if one takes into account the variety of structural and electronic phenomena in the course of reaction.

Wong et al. [105] investigated, by means of DFT calculations, the fundamental details regarding the synergy at the interface between Cu monomer or CuO dimer and $\text{CeO}_2(111)$ and its particular effect on CO oxidation. It was demonstrated that the synergistic effect at Cu–Ceria interface is comprised of electronic phenomena linked to

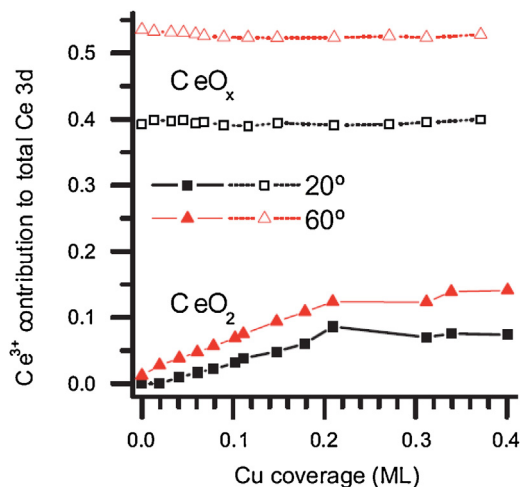


Fig. 9. Ce^{3+} contribution to the Ce3d core level spectra upon the deposition of copper to stoichiometric (CeO_2) and reduced (CeO_x) ceria films.

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electron transfer and distinct charge separation between Cu and CeO_2 (Fig. 10). In the case of Cu monomer there is an electron loss in Cu atoms and an electron gain in the O atoms of CeO_2 . In CuO dimer there is an electron loss in Cu atoms followed by an electron gain in the O atoms of CuO adlayer. Such electron modifications resulted in electron back-donation from Cu3d states to $2\pi^*$ anti-bonding orbital of CO, which stabilizes CO chemisorption on Cu sites. It was concluded that the existence of both Cu monomer and CuO dimer species on CeO_2 support is required for CO adsorption and consequent oxidation.

The nature of Oxide–Metal interactions in ceria-based coinage metals (Cu, Ag, and Au) inverse catalysts was thoroughly investigated by Graciani et al. [150], based on DFT calculations. The most stable and reduced CeO_x species were identified in $\text{CeO}_x/\text{Cu}(111)$ system, followed by $\text{CeO}_x/\text{Ag}(111)$ and $\text{CeO}_x/\text{Au}(111)$. The obtained results were rationalized on the grounds of geometric and electronic phenomena taking place at the interface. In particular, the low work function of Cu (4.94 eV) can be accounted for the charge transfer from the metal to the oxide towards the formation of reduced Ce^{3+} species. At the same time, the structural parameters of Cu(111) are more favorable, as compared to those of Ag(111) and Au(111), resulting in strong bonding interactions with the CeO_x towards the stabilization of Ce^{3+} species. These results unambiguously revealed that not only the properties of the metal but also of the oxide can be modified at the CeO_x –CuO interface, with great implications in catalysis (*vide infra*).

The origin of the high H_2O dissociation activity of CuO/ CeO_2 catalyst, which in turn boosts the rate of WGS reaction, was theoretically investigated by Yang et al. [129]. It was found that Cu clusters (Cu_x , $x=1-4$) tend to bind with the surface oxygen of $\text{CeO}_2(111)$ surface. The morphology of these clusters is determined by Cu–O interface bonds as well as by the population and strength of Cu–Cu bonds. The charge transfer from Cu to Ce results in positively charged Cu_x clusters, which demonstrated high H_2O dissociation ability as compared to unsupported clusters. It was inferred that CeO_2 has a pronounced effect on WGS activity by activating Cu sites through strong electrostatic interaction, but also by directly participating in the H_2O dissociation at the Cu–O interface. In a similar manner, theoretical calculations predict the existence of oxygen vacancies and edge atoms in ceria, which drastically enhance the reactivity towards CO, CO_2 , O_2 and H_2O molecules [38]. Szabová et al. [126] and Yang et al. [120] also shown by means of DFT+U calculations that ceria morphology has a significant impact on the electronic structure of interface and in consequence on H_2O disso-

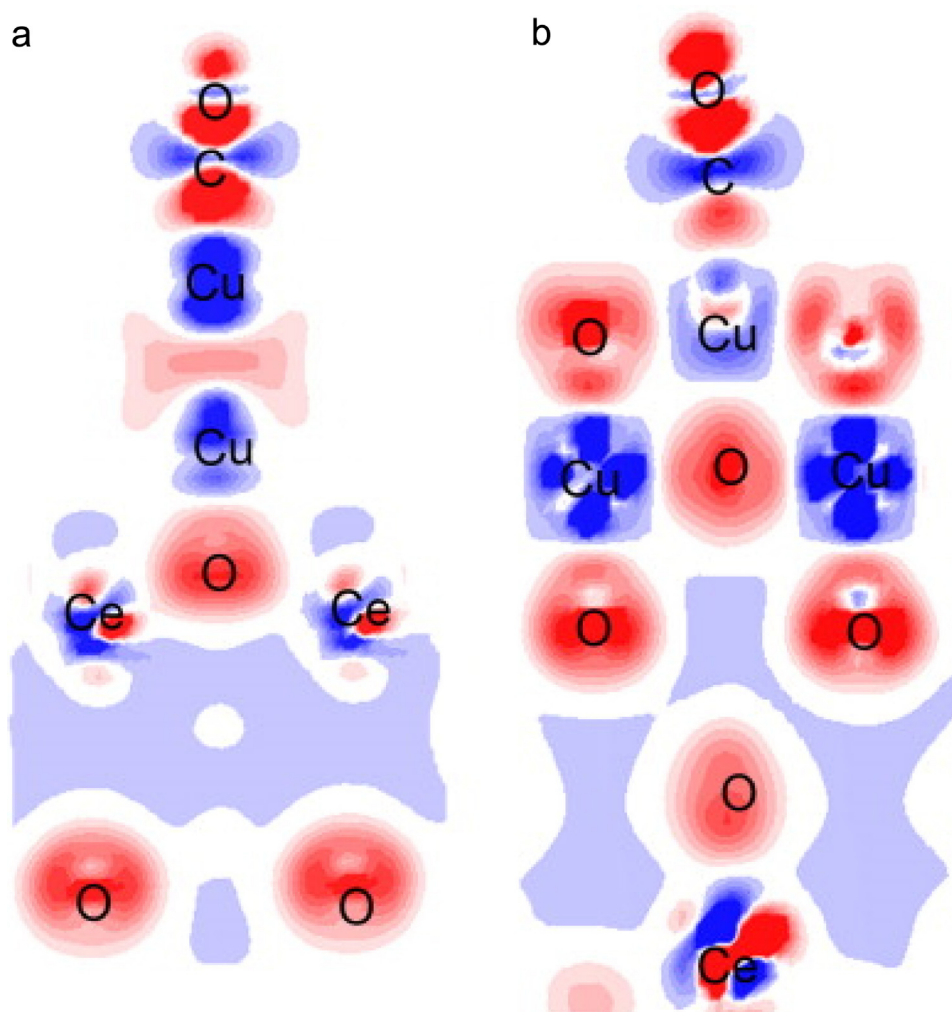


Fig. 10. Electron density difference plots of CO adsorbed on Cu monomer (a) and CuO dimer (b) modified CeO₂(111). Blue: electron gain; red: electron loss. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the original article. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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ciation. The latter is more pronounced when the ceria film thickness is below ca. 1.0 nm [126].

5. Inverse ceria/copper catalysts as a probing approach toward understanding metal–oxide interactions

In the light of the above considerations one can certainly affirm that metal–oxide interactions have a predominant role on the catalytic activity through mainly their impact on: i) the formation of Cu²⁺/Cu⁺(Cu⁰) and Ce⁴⁺/Ce³⁺ redox pairs, ii) the facilitation of reduction process as compared to individual CeO₂ and CuO counterparts, iii) the formation of surface oxygen vacancies, and iv) the stabilization of active intermediates at the interface. However, the extent of metal–support interactions is always affected by the surface, structural and morphological features of individual counterparts.

The need of a more thorough understanding at the molecular level of metal–oxide interface, stimulated the introduction of inverse catalysts, where the oxide nanoparticles are dispersed on metal surface, in opposite to conventional metal/support systems [38,39,43,46,47,128,142,158,164]. Inverse type catalysts have recently gained considerable attention, since they provide an excellent benchmark to understand the specific role of oxide particles

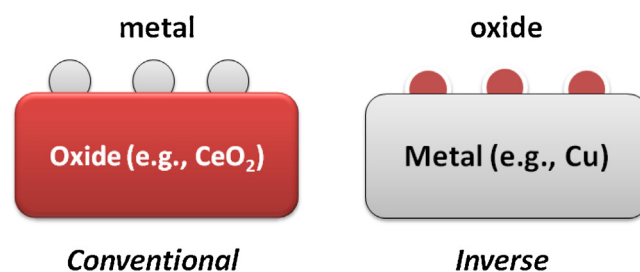


Fig. 11. Schematic representation of conventional versus inverse catalysts.

as well as of oxide–metal interfacial sites in catalytic properties. A schematic illustration of an inverse model catalyst versus to a conventional one is depicted in Fig. 11.

Several aspects in relation to the preparation of inverse ceria/copper catalysts and the surface reconstructions that can be induced by oxide deposition in metal surfaces were thoroughly discussed by Senanayake, Stacchiola and Rodriguez [38]. Herein, only some indicative studies are presented towards the fundamental understanding of Cu–Ceria interactions. To establish the importance of the physicochemical properties of oxide nanoparticle as well as of metal–support interactions, an inverse CeO_x/Cu(111)

system was *in situ* studied by IRRAS and AP-XPS under WGSR conditions [43]. The results revealed that no surface species other than CO were formed over bare Cu(111), in contrast to $\text{CeO}_x/\text{Cu}(111)$ catalyst, where the presence of adsorbed CO_xH_y species at the interface was established. These findings in conjunction to the fact that under WGSR conditions all the Cu is present as Cu^0 , while CeO_x nanoparticles have been reduced from $\text{CeO}_{1.98}$ to $\text{CeO}_{1.79}$, provides direct evidences on the impact of Cu–Ceria interactions on the formation of $\text{Cu}^{2+}/\text{Cu}^+$ (Cu^0) and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pairs under reaction conditions, which are directly involved in the dissociation of water. Remarkably, the situation is different in conventional supported catalysts, *i.e.*, CuO/CeO_2 , where the Ce^{3+} is a minority component, explaining the difference in activity (Fig. 4). In that case the defect sites present on oxide are partially covered by metal particles, limiting their pronounced effect [43,47].

Similar promotional effects through the adoption of inverse $\text{CeO}_x/\text{Cu}(111)$ catalysts have been obtained for the CO oxidation reaction [38]. This model system exhibited activities that are similar or even better than those obtained over highly active noble metals, such as Rh, Pd and Pt. It has been established that the supported ceria nanoparticles have special electronic and chemical properties, offering high O_2 dissociation activity. The O_{ad} derived by O_2 dissociation can then directly react with CO towards CO_2 formation, or spilled to copper surface towards CuO_x formation. Both these factors are considered crucial in the CO oxidation mechanism [38].

6. Structure–activity correlations (SARs) in relation to the recent advances on Cu–Ceria interactions

In this section some of the most relevant applications of CuO/CeO_2 catalysts are presented with particular emphasis on the role of Cu–Ceria interactions. It is not the aim at this section to provide an extended literature survey on the applications of CuO –Ceria oxides. This can be found in several relevant comprehensive studies in the field [3–6].

6.1. Preferential oxidation of CO in the presence of H_2 (CO-PROX)

The increase in demand for clean energy has boosted the interest towards proton exchange membrane fuel cells (PEMFC) due to their high efficiency and wide range of applications. Hydrogen fuel in combination with PEMFC constitute a viable energy alternative to both stationary and mobile applications. However, carbon monoxide which inevitably presents in the reformat gas mixtures is a strong poison for the low temperature H_2 –PEMFCs. Hence, its concentration must be kept below ca. 100 ppm in H_2 -rich stream which is used as fuel in PEMFC. The CO-PROX process has been recognized as one of the most effective methods to achieve this goal.

Among the numerous catalysts that have been examined for CO-PROX, the CuO/CeO_2 composites have demonstrated competitive levels of activity, selectivity and durability [4]. Therefore, CuO/Ceria catalysts have gained much attention, from economical but also from fundamental point of view. The superior catalytic performance of Copper–Ceria materials for CO-PROX has been attributed to the peculiar properties of Cu–Ceria interfacial sites, such as the excellent redox behavior, the formation of surface oxygen vacancies and the electron exchange between $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pairs. In the majority of the studies devoted on CO-PROX the above mentioned peculiarities have been considered as key factors to explain the high activity of CuO/Ceria catalysts, based mainly on indirect, *ex situ*, characterization studies. In contrast, direct evidences on the structural/electronic modifications that could take place under reaction conditions are rarely provided, limiting the establishment of rigorous SARs [4]. This is because it is necessary to combine advanced characterization techniques with *operando*

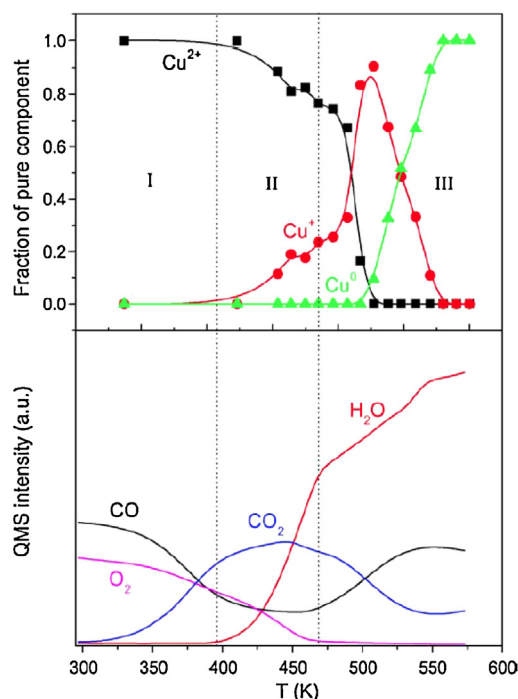


Fig. 12. Correlation of Cu species with the various gases detected in the course of the *operando* test with the XAFS cell.

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studies to gain insight into the molecular origin of the catalytic activity. Some recent advances towards this direction are described in the sequence.

The structure–activity relationship of Copper–Ceria catalyzed PROX reaction was thoroughly investigated by Martínez-Arias and co-workers by means of detailed structural and electronic characterizations [7,10,17,24,26,28,29,165]. A comprehensive review on the subject has been also lately published by the same authors [4]. In brief, *ex situ* characterization studies in conjunction with *operando* spectroscopic evidences by DRIFTS and XANES clearly revealed that significant changes on Cu and ceria surface chemistry can be produced in the course of reaction. In particular, *operando* spectroscopic analysis revealed the pronounced impact of ceria on the reduction of Cu species at the interfacial sites, which are the active entities for CO oxidation. A direct correlation between the Cu^+ -carbonyls intensity and the CO oxidation rate was established (Fig. 12) [17]. In complete agreement, Polster et al. [34] and Yang et al. [35] proved by means of *in situ* DRIFTS studies that the CO oxidation activity is linked to Cu^+ -carbonyls species. More importantly, the extension of the reduction over the Cu sites not strongly associated with ceria, provides the most active sites for the undesired H_2 oxidation process [4,10,35].

In the light of these findings, it has been proposed that the possible separation of the two types of copper sites, *i.e.*, partially and highly reduced copper entities, could open new horizons towards controlling the two competitive oxidation processes [4]. Under this perspective, it has been recently shown that by changing the geometric type of interactions between copper and ceria (*e.g.*, by employing different ceria morphologies, inverse configurations, *etc.*) ones can tune the interfacial interactions and in turn the CO-PROX activity [11,29,31,165]. In view of this fact, a wider CO conversion window and higher CO_2 selectivity was achieved by inverse CeO_2/CuO catalysts in comparison to conventional CuO/CeO_2 [31]. This was related to the limited reducibility of larger size CuO particles in inverse catalysts, as directly demonstrated by means of *operando* studies [31]. Similar conclusions have

been drawn by several groups, e.g., [12,32,166,167]; inverse catalysts can provide large, not easily reduced, CuO crystallites at the periphery of CeO₂–CuO interface, thus favoring the CO oxidation at the expense of H₂ oxidation.

The impact of synthesis procedure on the CO-PROX behavior was extensively investigated by many research groups, e.g., [8,15–17,19,20,23,27,30,33,36,167–185]. Various preparation methods, involving impregnation, precipitation, hydrothermal, chelating, urea-nitrates combustion, nanocasting, etc. have been employed. Significant structural and morphological modifications are induced by the synthesis route, reflected then on PROX performance. In general, the formation of nanostructured composites with large surface area and optimal concentration of oxygen vacancies promotes the interaction between Cu and ceria, which in turn facilitates the formation of highly active Cu⁺ species. Interestingly, the incorporation of Mn and Fe dopants into CuO/CeO₂ composites resulted in the formation of more Cu⁺ species and oxygen vacancies, with a beneficial effect on PROX activity [186]. This is of major importance, opening new horizons towards the fine-tuning of Cu–Ceria catalysts by means of structural and/or surface promotion [135].

Moreover, the impact of ceria morphology on PROX activity was investigated by Han et al. [18], by employing different shapes of ceria supports (i.e., rods, cubes, and octahedra). The CuO/ceria–octahedra showed the highest activity, which is ascribed to the higher surface content of copper in octahedra. Except the above mentioned shape effects, several other factors, such as the surface area, the copper dispersion and reducibility are considered to be involved in the PROX process, revealing the multifaceted phenomena that take place concurrently under reaction conditions. Very recently, the key role of highly dispersed CuO_x clusters on the PROX activity was revealed by means of *in situ* XAFS [13].

6.2. Water–gas shift reaction (WGS)

Hydrogen economy is regarded as a potential alternative to satisfy the increasing energy demands, contributing also to the stabilization of global climate by reducing greenhouse gas emissions. WGS reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is closely involved in reforming reaction schemes, consisting an important process to adjust the CO/H₂ ratio of the produced syngas. It is thus a subject of substantial interest in both industrial and academic research.

CuO/CeO₂ is one of the most widely studied catalysts because of its outstanding WGS performance as well as due to the fundamental knowledge that can be gained by understanding the origin of WGS activity at atomic level. Although it is generally recognized that the strong interaction between Cu and ceria is the starting point of the enhanced WGS activity, details of this interaction at atomic level are still unclear. Hence, the WGS reaction over CuO/Ceria catalysts has become a benchmark system for studying the nature of Cu–Ceria interactions.

Two different reaction mechanisms have been generally proposed for CuO/Ceria-catalyzed WGS reaction. The first one, the so-called *redox mechanism*, involves the oxidation of adsorbed CO by the atomic oxygen provided by H₂O dissociation. The second one, the *associative mechanism*, entails the formation of several intermediate species, such as formates, carbonates and carboxyls, which are originated by the reaction of CO with surface hydroxyl groups, e.g., [46,54,55]. Although the role of copper and ceria and in particular of their interaction is still a matter of debate, it is commonly believed that the dissociation of H₂O is the rate-determining step. Several questions, however, regarding the complicated Cu–Ceria synergistic effects are still open: what is the origin of the high H₂O dissociation ability of CuO/Ceria system? Which are the active sites under reaction conditions? Despite the fact that the answer on these questions lies behind the com-

plicated Cu–Ceria interactions, the fundamental understanding of the underlying mechanisms at atomic level is an open issue. Many factors, involving mainly the shape, the size and the dispersion of copper and ceria particles affect the WGS activity.

Significant progress on the fundamental understanding of the underlying mechanisms of Copper–Ceria interactions with respect to WGS reaction has been performed by Rodriguez and co-workers. They clearly showed by means of *operando* studies over both conventional and well-defined model systems the formation of reduced copper (Cu⁺/Cu⁰) and cerium (Ce³⁺) species under reaction conditions, stabilized through metal–support interactions [40–43,45–47,56,164]. Moreover, the stabilization of CO₂^{δ−} species at the Cu–Ceria interface is revealed, in contrast to bare Cu(111) surface which is predominated by CO_{ads} species. This explains the superior WGS activity of CeO_x/Cu(111) system as compared to the low active Cu(111) (Fig. 4) [43,46].

Moreover, Flytzani-Stephanopoulos and co-workers [44] clearly shown by means of XANES that at temperatures where the WGS reaction is taking place, the Cu²⁺ entities were progressively reduced to Cu⁺/Cu⁰ species, implying the key role of reduced Cu species for WGS activity (Fig. 7). These species are related to strongly bound Cu–[O_x]–Ce ligands, associated with the surface oxygen vacancies of ceria. In contrast, weakly bound CuO_x clusters and CuO nanoparticles were found to be spectator entities.

It should be noted, however, that although Copper–Ceria interactions have significant implications on WGS activity, their extent depends on several interrelated factors, such as support defects and imperfections, morphology, particle size, copper dispersion, etc. In this respect, a direct correlation between the ceria geometric features and WGS activity was established [51,56,187]. For instance, ceria nanospheres demonstrated higher WGS activity, as compared to ceria nanocubes, due to their unique properties, such as the easier reduction of highly dispersed CuO to Cu⁰ and the higher population of Ce³⁺ species [51]. In a similar manner, it has been shown by both theoretical [38,120,126,129] and experimental [154–157] studies that both ceria and copper morphology affect the electronic structure of interfacial sites and thus their WGS activity.

The strong correlation between the WGS activity and the morphological characteristics of catalysts has stimulated the research interest towards the employment of different synthesis routes, pre-treatment protocols and Cu/Ce atomic ratios, e.g., [49,52,53,188–193]. The ultimate target is always to obtain the optimal geometric characteristics, which in turn can boost the interfacial activity.

6.3. Methanol synthesis

CO₂ hydrogenation to alcohols or hydrocarbons is a key process to mitigate CO₂ emissions and to synthesize valuable commodities, such as methanol. The unique role of Cu–Ceria interface during the CO₂ hydrogenation to methanol over CuO/CeO₂ catalysts in catalysis has been recently confirmed [57–60,153]. Rodriguez and collaborators proved by means of both experimental studies and theoretical calculations that the combination of metal and oxide sites in the Cu–Ceria interface can facilitate the CO₂ conversion to methanol [57,60]. The latter is of major importance taking into account the difficulties associated with the chemical inertness of CO₂.

Fig. 13 compares the activity of different Cu-based composites for methanol synthesis. Bare Cu(111) exhibited very low activity. In contrast, CeO₂/Cu catalyst is much more active for methanol synthesis than both bare Cu and Cu/ZnO. By means of ambient-pressure XPS and IRRAS studies it was found that CO₂ was not adsorbed on bare Cu, whereas strongly bound carbonates (CO₃^{2−}) were identified on CeO₂(111). In contrast, Cu–Ceria interface resulted to the formation of carboxylate species (CO₂^{δ−}). The latter species have

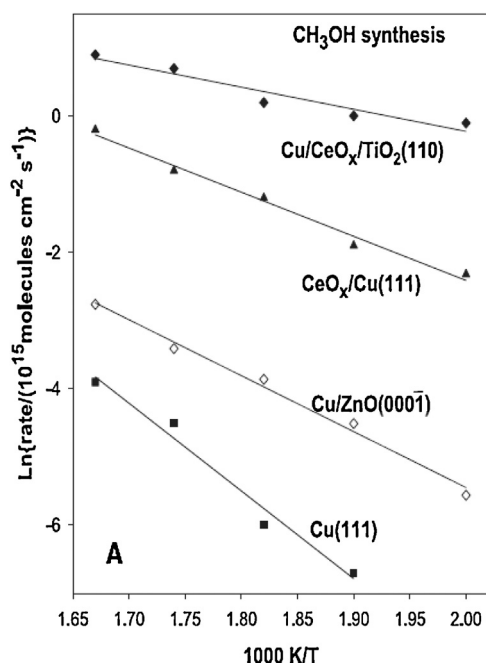


Fig. 13. Arrhenius plot for methanol synthesis on Cu, Cu/ZnO, CeO_x/Cu and Cu/CeO_x/TiO₂ catalysts. Reaction conditions: 0.5 atm of CO₂ and 4.5 atm of H₂.

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lower stability than the strongly bonded formate species, being active intermediates for methanol synthesis.

Similarly, earlier studies revealed the potential of CuO/CeO₂ catalysts in methanol synthesis from CO hydrogenation. In particular, Shen et al. [58] found that CuO/Ceria catalysts are more active in CO hydrogenation than conventional Cu/ZnO catalysts. The *in situ* formation of ionic copper species (Cu⁺), stabilized on catalyst surface via Cu–Ceria interactions, were thought to be responsible for the high methanol synthesis activity. The importance of metal–oxide interfaces on the CO₂ hydrogenation to methanol has been very recently reviewed in a comprehensive manner by Rodriguez et al. [57].

6.4. CO oxidation

CO oxidation reaction is probably one of the most well-studied reactions in heterogeneous catalysis, due to its fundamental and practical importance. The catalytic abatement of CO is of particular importance in several technological areas, involving among others automotive pollution control and fuel cell applications. More importantly, the CO oxidation reaction can provide a unique benchmark to gain insight into the structure–activity correlations.

Copper–Ceria catalysts have gained considerable attention on this reaction, serving as an ideal replacement of NMs-based catalysts. The impact of Cu–Ceria interactions on CO oxidation activity was thoroughly investigated by employing different: i) ceria morphologies [97,100,103,106,194–199], ii) synthesis routes [3,99,200–212], iii) metal oxides precursors [100,197,203,213], and iv) inverse configurations [38,94,95,101].

It was clearly revealed, by employing an inverse CeO₂/Cu configuration, that the deposition of ceria nanoparticles (NPs) in Cu(111) substrate substantially enhanced the activity as compared to bare Cu [38]. Activities comparable or even higher than those reported for Rh, Pd and Pt metals were found. The origin of this extraordinary activity was attributed to the high O₂ dissociation activity of ceria NPs and the subsequent spillover of O_{ad} to Cu. The interaction of CO_{ad} with O_{ad} species located either on ceria or Cu substrate can be

accounted for the high oxidation activity [38]. DFT calculations further supported the high oxidation ability of ceria NPs due to their particular electronic properties [94]. In a similar manner, DFT+U calculations have revealed that only physisorbed CO species can be formed on the clean ceria(111) surface, in contrast to Cu-doped ceria, where both physisorbed and chemisorbed CO_x species were observed [102]. Moreover, it has been found by means of photoemission spectroscopic studies that the lowering of the CO oxidation temperature upon the Cu loading on ceria can be explained by the CO adsorption on Cu sites in the vicinity of oxygen-rich ceria planes [101].

Copper-modified ceria nanospheres, fabricated by hydrothermal synthesis, demonstrated excellent low-temperature CO oxidation [97]. The latter was attributed to the coexistence of Ce⁴⁺/Ce³⁺ and Cu²⁺/Cu⁺ redox couples, the formation of oxygen vacancies and the stable existence of Cu⁺ species under reaction conditions. In this regard, the superior CO oxidation activity of Ce³⁺-based catalysts as compared to the Ce⁴⁺-based catalysts has been reported in [213]; Ce³⁺ species shift the redox equilibrium of Cu²⁺ + Ce³⁺ ⇌ Cu⁺ + Ce⁴⁺ to the right, thus promoting the formation of highly active Cu⁺ species [3,213–216].

Zhou et al. [104] investigated the impact of ceria morphology (nanorods or nanoparticles) on the local surface structure and CO oxidation activity of Cu-based catalysts. CeO₂ nanorods provided a more favorable synergetic effect with CuO, resulting in excellent reducibility which is linked to Cu²⁺/Cu⁺ transition. The latter was considered responsible for the superior CO oxidation activity of CuO/CeO₂-nanorods compared to CuO/CeO₂-nanoparticles.

Moreover, several other factors, such as the synthesis route, the copper precursor and the calcination temperature can exert significant modifications on the dispersion and the consequent interaction of CuO species with CeO₂ [96,98,100]. For instance, three different CuO species have been identified on nanosized CuO–CeO₂ catalysts: finely dispersed CuO species, bulk CuO and CuO in CeO₂ lattice. Amongst these species the finely dispersed CuO can induce the most favorable synergistic CuO–CeO₂ interactions upon high-temperature calcination or under reaction conditions towards the formation of highly active Cu⁺ species [98,100]. Furthermore, it was demonstrated that the synergistic effect at Cu–Ceria interface is comprised of electronic phenomena linked to electron transfer and distinct charge separation between Cu and CeO₂. Such electron modifications resulted in electron back-donation from Cu3d states to 2π* antibonding orbital of CO, which stabilizes CO chemisorption on Cu sites [105].

Recently, Elias et al. [106,217] followed a novel synthesis approach for the preparation of monodisperse, phase-pure nanocrystals of Cu_yCe_{1–y}O_{2–x} composites. Contrary to the above findings, a surface-substituted Cu_yCe_{1–y}O_{2–x} phase, instead of Cu⁺/Cu²⁺ species, was considered as the active phase involved in the low temperature CO oxidation [217]. It was revealed, by means of *in situ* XAS measurements, that copper ions in Cu_yCe_{1–y}O_{2–x} phase are stabilized at high oxidation state (Cu²⁺ and Cu³⁺) without evidences on the formation of Cu⁺ species. According to the authors, however, the possibility of the existence of undetectable, highly active, Cu⁺ species cannot be ruled out. Moreover, the enrichment of catalyst surface in Ce³⁺ species, correlated with surface oxygen vacancies, was considered crucial for the enhanced catalytic activity of Cu_yCe_{1–y}O_{2–x} composites. These findings clearly demonstrated the crucial role of synthesis procedure on the solid state properties of as prepared materials and their implications in catalysis. The novel synthetic strategy adopted by Elias et al. [106,217], lead to the formation of monodisperse nanoparticles, may be accounted for the aforementioned contradictions in relation to the active sites for CO oxidation. Nevertheless, it is evident,

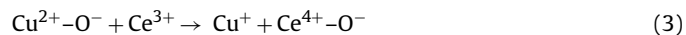
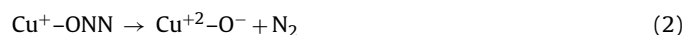
that further mechanistic studies are required towards a rigorous structure–activity correlation.

6.5. N_2O decomposition

Nitrous oxide (N_2O) has been recently recognized as one of the most powerful greenhouse gases and ozone depleting substances [135]. Therefore, its effective abatement in tail-gases is of major environmental importance. Although NMs-based catalysts exhibit a satisfactory deN_2O performance, their high cost and sensitivity to various off-gases (e.g., O_2 , H_2O) limit their practical applications. In view of this fact, NMs-free mixed oxides have received considerable attention as potential alternatives. Among them, CuO/CeO_2 catalysts are lately at the forefront of research due to their unique properties linked to Cu–Ceria synergistic effects [88–93,135].

The recent advances in the field of N_2O decomposition over metal oxides have been recently reviewed by Konsolakis [135]. Several issues concerning the N_2O decomposition mechanism as well as the strategies that can be followed to adjust the local surface structure of oxidic catalysts have been addressed. It has been clearly addressed that the N_2O decomposition over mixed oxides, such as CuO/CeO_2 catalysts, follows a redox-type mechanism, involving at first dissociative chemisorption of N_2O to N_2 and O_{ads} , followed by the recombination of adsorbed oxygen species to gaseous O_2 . The key role of Cu–Ceria interactions on the above mechanistic sequence are shortly discussed in the sequence.

To gain insight into the particular role of CeO_2 as well as of Cu–Ceria interactions on the de N_2O performance, three different types of materials, namely: (i) bare CeO_2 , (ii) CuO/CeO_2 oxides by deposition of CuO phase on CeO_2 support iii) single stage synthesized CuO/CeO_2 mixed oxides, have been recently prepared by Konsolakis et al. [91]. In all the examined cases ((i)–(iii)), impregnation, precipitation and exotemplating methods were employed. The optimum performance was obtained for the CuO/CeO_2 mixed oxides prepared by co-precipitation, offering complete N_2O conversion at 550°C . At this temperature, conversions lower than 20% were obtained for bare CeO_2 . On the basis of characterization studies (micro-Raman, XPS, TPR) it was revealed that the superiority of CuO/CeO_2 mixed oxides prepared by precipitation can be ascribed to their excellent reducibility related to the facilitation of $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ redox cycles. A redox mechanism involving the N_2O adsorption on Cu^+ sites and their subsequent regeneration through Cu–Ceria interactions was suggested:



The relative abundance of Cu^+ and Ce^{3+} species in samples prepared by co-precipitation, as revealed by XPS and Raman analysis, is in accordance with the synergistic copper and ceria interactions, which facilitates the redox cycles between $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ pairs and in turn the deN_2O performance [91]. In a similar manner, it was revealed by means of *in situ* DRIFTS studies and DFT calculations that the synergistic Copper–Ceria interaction promotes the formation of Cu^+ , which accounts for the high deN_2O activity of CuO/CeO_2 catalysts [88,92,93]. The impact of ceria morphology (nanocubes, nanorods, nanopolyhedra) on the deN_2O performance of CuO/CeO_2 catalysts was thoroughly investigated by Zabilskiy et al. [90]. CuO supported on CeO_2 nanorods demonstrated the lowest activation energy for N_2O decomposition, due to their superior oxygen mobility and their ability to regenerate the Cu active sites. The key role of $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$ sites in catalytic N_2O decomposition pathway was recently revealed by means of *operando* studies [218].

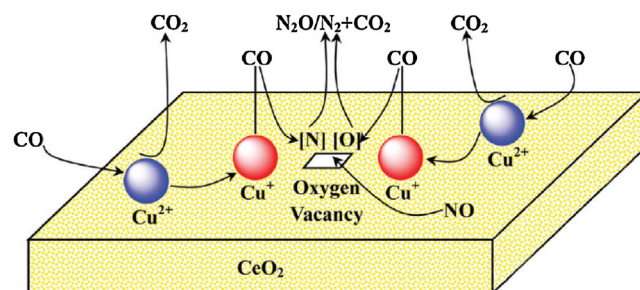


Fig. 14. Proposed reaction model of NO reduction by CO over CuO/CeO₂ catalysts. Reproduced with permission from Ref. [79]. Copyright© 2013, Royal Society of Chemistry.

6.6. Selective catalytic reduction (SCR) of NO

Nitrogen oxides (NO_x) emitted from mobile and stationary sources during fossil fuels combustion is a matter of growing concern worldwide. The selective catalytic reduction (SCR) of NO by NH_3 is one of the most effective methods for controlling NO_x emitted from stationary sources. Moreover, the catalytic reduction of NO by CO or hydrocarbons is among the most important reactions in TWCs, with a predominant contribution on exhaust gases purification.

Vanadium-based commercial catalysts, which are employed for the NO_x abatement from stationary sources, are active within a narrow temperature window, encountering also toxicity issues [219]. On the other hand, the platinum group metals (PGM), which are extensively applied in TWC technology, are rather expensive. Hence, the development of low-cost and efficient catalysts for the NO_x abatement is of great importance in environmental catalysis. Among the various transition metal-based catalysts, the Cu-ceria system is gaining tremendous attention. The recent developments on the role of Cu-Ceria interactions in the SCR process are discussed below.

The impact of the ceria morphology on the SCR activity of CuO/CeO₂ catalyst was investigated by Liu et al. [220]. Ceria nanopolyhedra, nanorods and nanocubes were employed as supporting carriers. The optimum NO reduction activity was obtained with Cu supported on nanorods, due to the strongest interactions between Cu and CeO₂. In particular, the synergistic interaction of CuO with the (110) plane of ceria nanorods enhanced the oxygen defect concentration and facilitated the redox equilibrium between Cu²⁺ and more reduced copper species (Cu⁺/Cu⁰); both factors are considered crucial in the NO reduction mechanism.

The influence on the preparation method on the solid state properties and in turn on the SCR of NO by CO of CuO/CeO₂ samples was systematically investigated by Yao et al. [79]. A correlation between the concentration of surface oxygen vacancies and low valence copper species with the catalytic activity was revealed. Oxygen vacancies facilitate the NO dissociation, whereas the reduced copper species are considered responsible for CO adsorption (Fig. 14) [79,84].

Jiang et al. [81] reported on the room temperature SCR of NO by urea over carbon-fibre-supported CuO/CeO₂ oxides. A synergistic effect between highly dispersed Cu and Ce species was considered responsible for the formation of Ce⁴⁺/Ce³⁺ and Cu²⁺/Cu⁺ redox pairs, which are involved in the SCR process. In an attempt to elucidate which copper sites possess the highest catalytic activity during the NO SCR process, Zheng and co-workers synthesized Cu/CeO₂ catalysts treated with nitric acid. The purpose was to remove CuO crystallites not strongly interacting with ceria [82]. Interestingly, both un-treated and nitric acid-treated catalysts demonstrated comparable NO conversion, despite their extremely different Cu loading, *i.e.*, 0.27 vs. 5.0 wt.%. On a basis of a complimentary spec-

troscopy study it was shown that three copper entities, *i.e.*, copper localized in octahedral sites of ceria, copper oxide clusters and copper in surface substitutional sites, are involved on the SCR process.

7. Outlook and challenges

In the present survey, the latest advances on the origin of Copper–Ceria interactions and their implications in catalysis were summarized. Fundamental insights lately obtained by means of *in situ* or *ex situ* characterization techniques, theoretical studies (DFT calculations) and innovative probing approaches (inverse CeO₂/CuO system) were provided. Indicative applications of CuO/CeO₂ binary oxides in catalysis, such as the WGS, CO-PROX, SCR, CO₂ hydrogenation, CO oxidation, and N₂O decomposition processes, were outlined, with particular emphasis on the role of Cu–Ceria interactions. In summary, the following concluding remarks can be drawn.

CuO/Ceria binary oxides have found numerous applications in energy and environmental catalysis due to their unique catalytic features and lower cost as compared to NMs-based catalysts. On the basis of the most instructive experimental and theoretical studies, the superior reactivity of Cu/Ceria catalysts can be in principle correlated with a synergistic effect linked to Cu–Ceria interactions. Various interrelated phenomena were found to be at work at Cu–Ceria interface, with great consequences on the catalytic activity:

- (i) modification of local surface chemistry *via* the electronic perturbations induced by bonding interactions between Cu and Ce nanoparticles;
- (ii) facilitation of the redox interplay between Cu²⁺/Cu⁺ and Ce³⁺/Ce⁴⁺ couples;
- (iii) formation of surface defects, such as oxygen vacancies;
- (iv) enhanced reducibility;
- (v) interfacial reactivity, *i.e.*, the unique activity which give rises at the metal–support interface.

It can be inferred that the Cu–Ceria interface can offer multifunctional sites with distinctive chemical characteristics, difficult to be obtained over their bare counterparts. In this regard, the fine-tuning of both copper and ceria oxides morphological characteristics (mainly morphology and particle size) can notably affect the metal–support interactions and in turn the performance of the interface. In particular, the formation of nanostructured composites is of significant importance, given the strong electronic interactions between nanoparticles. The latter is of major importance, opening new horizons for the development of highly dispersed and applicable metal/oxide or oxide/metal systems with modulated properties. In this direction the employment of advanced synthetic routes could trigger unique opportunities towards the development of specific architecture catalysts with the desired properties. Furthermore, the adjustment of the surface chemistry and structural defects of Cu–ceria binary system by means of electronic and/or structural promotion (*e.g.*, the addition of alkali or alkaline earth modifiers) could boost the interfacial reactivity.

Moreover, the complex solid–solid (*e.g.*, expose of different crystal planes, electronic perturbations) and solid–gas (*e.g.*, formation of active or spectator adsorbed species) interactions under real working conditions, introduced a great difficulty to unambiguous reveal the origin of catalytic effects and to establish a definite structure–activity correlation. To this end, complimentary characterization studies are required to understand the fundamental origin of the catalytic activity.

As a general remark, the results presented in this review can be used as a guideline for the development of novel Cu-based

composites for several energy and environmental applications. The fine-tuning of local surface structure by means of nano-synthesis routes and/or structural/electronic promotion could lead to highly active and stable catalysts. In any case, the fundamental understanding at atomic level of metal–support interactions is a *conditio sine qua non* for the rational design of highly efficient and inexpensive catalysts.

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